Multi-Beam Engineering Microscopy - a Versatile Tool for Optimal Materials Design

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Abstract — **Engineering microscopy is a term we use to refer to a suite of versatile techniques for spatially resolved characterisation of material structure and properties for the purpose of optimising design, performance and durability of structures and technological systems. The range of tools that can be used for this purpose includes beams of photons (including X-rays), electrons, neutrons, and ions. Different modes of imaging include absorption and emission, spectroscopy, and scattering that can be used in full field or scanning regimes. The approaches that collect information in the form of 2D images can also be extended to 3D characterisation by serial sectioning or reconstruction tomography. An important additional mode of near-surface property evaluation arises through the use of nanoscale contact tip sensors, such as AFM, nanoindentation, electrochemical probes, etc. Crucial underpinning for multi-beam microscopic characterization is provided by multi-scale materials modelling.**

The lecture will provide an overview of flavours of engineering microscopy and highlight the exciting opportunities presented by the combination of techniques in the form of so-called correlative microscopy. Examples of multi-modal correlative microscopy will include partially stabilized zirconia, biomaterials such as flax fibres and human dental tissues, and also advanced engineering alloys and ceramics."

***Index Terms*—SiC fibre, FIB-SEM microscopy, Raman spectroscopy.**

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I. Introduction

MULTI-BEAM engineering microscopy is a new concept in materials characterization that serves the purpose of optimal engineering design at the micro- and nano-scale. What makes this term appropriate is the fact that most microscopy techniques make use of some form of a beam: photons, electrons, ions or neutrons. Ironically, even AFM, the technique for nano-scale imaging that relies on a fundamentally different principle, namely, the interaction between a sharp tip and the sample surface to form an image also makes use of a cantilever *beam* to convert the tip displacement into measured signal.

In this paper we wish to report and illustrate the development of our facilities and capabilities at MBLEM, the Multi-Beam Laboratory for Engineering Microscopy at Oxford. The suite of instruments that we use is built on the platform provided by the Tescan FIB-SEM instrument LYRA-3XM equipped with SE, BSE and STEM electron detectors, and enhanced with the Oxford Instruments Nordlys Nano® EBSD and EDX micro-analysis systems. Since these additional characterization tools are not yet available at Oxford, we make use of the in-SEM Raman micro-spectroscopy and FIB-based TOF-SIMS analysis tools at Tescan’s Brno headquarters. In addition to these capabilities we make use of the in-house X-ray facilities (Bruker D8 diffractometer with VÅNTEC 2000 area detector, and two Yxlon 160kV W-tube 2.25kW industrial imaging sources), as well as synchrotron X-ray beamlines at Diamond Light Source at the nearby Harwell Oxford campus.

The combination of different imaging approaches applied to the same region of interest within the material we wish to interrogate allows us to derive insights into the structure and function that otherwise would not be possible.

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As an example we present here the results of the investigation concerning the structure, grain size, orientation and residual stress within silicon carbide fibres with carbon monofilament cores that provide continuous uniaxial reinforcement for titanium alloy Ti-6Al-4V used in the manufacture of "blisks" (bladed disks) for aeroengines [1].

II. MATERIALS AND METHODS

A. *Material structure and sample preparation*

The exceptional mechanical properties of SiC fibres (strength and stiffness) make them eminently suitable for reinforcement of metal matrix composites. This application of these fibre systems is the principal interest here, although their use in ceramic matrix composites is also acquiring growing significance. The common design objective is the optimization of the performance of individual fibres, as well as entire material systems that incorporate them as the principal load-bearing element. In order to achieve this objective, the investigation of the microstructure-property relationships is crucial. Considering the fact that the key constitutive elements or features of the fibres have dimensions in the (sub)micron scale, suitable high resolution probes must be used.

One type of SiC fibres widely available commercially is the so-called SCS series of SiC fibers (Textron Specialty Materials, Lowell, MA). The fibres are manufactured by chemical vapour deposition of SiC on a carbon filament. Historically, the earlier types of fibres produced in this way had a ~50μm-thick layer of SiC deposited on a carbon core of ~30μm diameter, resulting in fibres of ~130μm outer diameter. The fibres produced in the more recent years have had an outer carbon-based coating applied for incorporation into titanium alloy matrices, or carbon- and titanium boride coatings for aluminium alloy matrices.

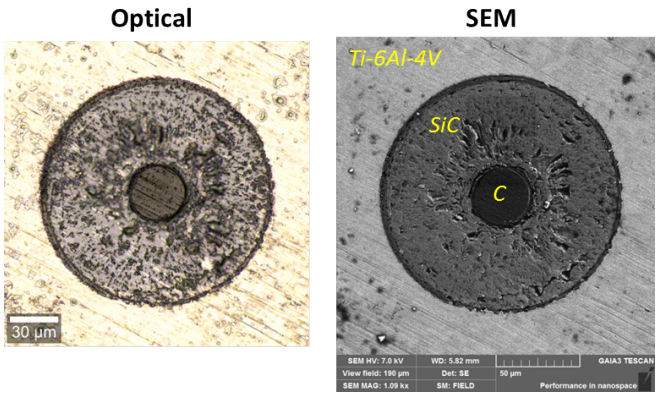

Fig. 1. Micrographs of SiC fibre architecture obtained using (a) optical microscopy, and (b) SEM. The carbon filament core, CVD-deposited SiC layer and the Ti-6Al-4V matrix are identified. The dark interlayer between SiC and the surrounding matrix is the carbonaceous coating applied to promote adhesion.

In the 1990's the process was developed for SiC fibre pre-coating with titanium alloy prior to consolidation into the uni-directionally reinforced composite. In this process the metallic target with a suitable composition close to that of the matrix alloy was subjected to electron beam evaporation in a chamber containing a rotating fibre carrier [1]. As a result, Ti alloy coatings a few tens of microns thick were produced. The final consolidated composites were obtained by hot isostatic pressing (HIP) at temperatures between 500°C and 925°C with the desired fibre volume fraction achieved by the addition of alloy matrix powder.

Fig. 1 presents images of the structure of the metal matrix composite material using in this study obtained by optical and electron microscopy. The composite material was supplied by Advanced Metal Composites (AMC Ltd., Farnborough, UK). The darker central region visible in both images is the carbon filament core. Around it can be seen the layer of SiC that was deposited by chemical vapour deposition and possesses a pronounced directional character, with the radial growth direction clearly distinguishable. The surrounding Ti-6Al-4V matrix contains a transition (not immediately apparent from the micrographs presented) from the Ti alloy pre-coating layer to the matrix proper that is formed during consolidation. The dark carbon-based adhesion interlayer is visible between SiC and the alloy matrix.

B. *Correlative SEM-Raman microscopy setup*

The exceptional multi-modal mapping capability of correlative microscopy derives from the ability to combine and collocate Scanning Electron Microscopy (SEM) with confocal Raman imaging (CRM). This technique (sometimes referred to as RISE microscopy) was developed through the collaboration of Tescan (Brno, Czech Republic) and WITec Gmbh (Ulm, Germany). Three-dimensional (3D) schematic model of the illustrative parallel instrumentation setup is given in Fig. 2.

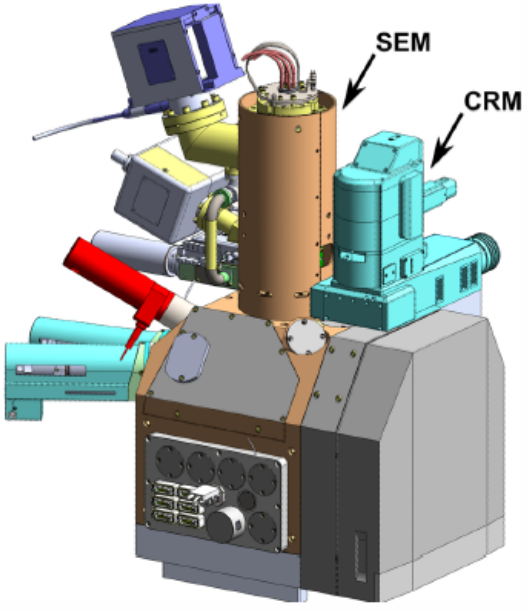

Fig. 2. Pseudo-3D schematic view of the possible parallel instrumentation setup that combines different imaging modalities within one chamber on the SEM platform [4].

The sample is firstly imaged in the SEM mode to obtain information about the electron density and topography of the sample surface. The sample is then automatically translated by a precisely defined displacement to present it for confocal Raman imaging within the same vacuum chamber

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of the electron microscope. The same region of interest at the sample surface is then scanned in the Raman imaging mode. At each image pixel a complete Raman spectrum is recorded that contains information about the molecular structure of the material. Raman images can be colour-coded on the basis of the intensity of certain bands within the Raman spectrum. These raster scans can be made semi-transparent and overlaid on the SEM micrographs, thus providing rich multi-layer images of material surface containing information about its molecular composition.

C. *Synchrotron X-ray imaging and micro-focus diffraction setup*

Synchrotron X-ray beams possess the combination of properties required for high-resolution imaging and characterization of samples of such materials as SiC fibres with carbon filament cores. The setup used for the study of the SiC fibre reinforced Ti-6Al-4V matrix composite is illustrated in [3]. The versatile setup allowed the combination of imaging and micro-focus diffraction scanning.

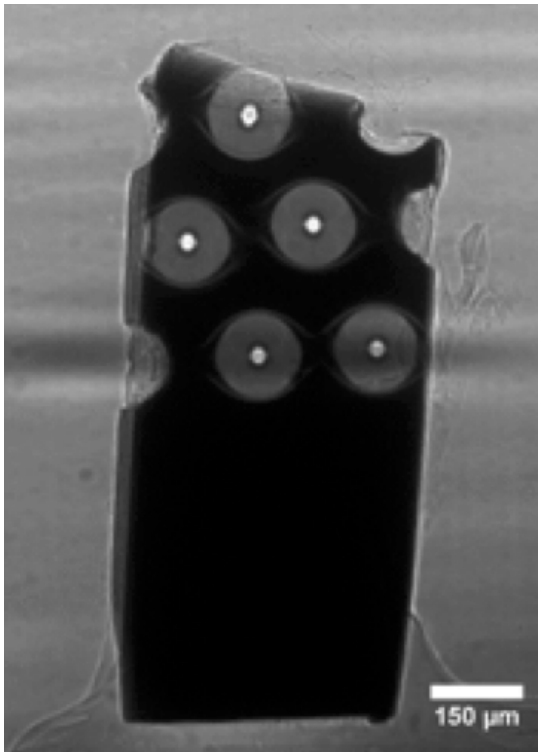

Fig. 3. Synchrotron X-ray radiogram of the small sample of Ti-SiC composite section aligned so that the incident beam is parallel to the fibre. The bright central cores of low absorption carbon filament are apparent (adapted from [3]).

Fig.3 shows a radiogram of the small sample of SiC fibre composite taken with the incident beam that was monochromated to 18keV and closely aligned with the direction of the fibre extent. This high precision alignment was essential to ensure that the incident beam illuminated a pencil-shaped gauge volume within the sample that allowed the mapping problem to be considered two-dimensional.

It is important to note that, unlike the near-surface, reflection mode microscopy techniques, such as SEM, and also Raman (with the typical penetration depth of a few microns), the penetrating power of high energy synchrotron X-rays means that the sampling volume extended through the full depth of the sample (~30µm). Nevertheless, close relationship can be established between these bulk and surface probes, provided appropriate alignment is assured. The results are presented below.

III. Results

A. *Correlative Raman spectro-microscopy mapping*

The Raman image (Fig. 4a) was collected in the area of 160×160 µm^2 (1µm/pixel) that contains 160×160 pixels= 25600 spectra. For each pixel, 1024 channels were used to store the data covering the wavenumber range between 32cm^{-1} and 3892cm^{-1}. The different colors in the Raman images illustrate the various molecular bonds identified within the sample by their vibration peaks. The relationship between this vibration "signature" of material bonds and the underlying SEM image is illustrated in Fig. 4b, where the semi-transparent Raman and SEM images are superimposed.

The spectrum types that are associated with the different colours are identified in Fig. 4c. Specifically, the pink spectrum represents the highly crystalline graphite with the D* peak; the grey spectrum represents partly amorphous graphite; the yellow spectrum is associated with the presence of the SiC peak at 796cm^{-1}; whilst the green, blue and red spectra reflect the different portions of the profile where carbon peaks are located.

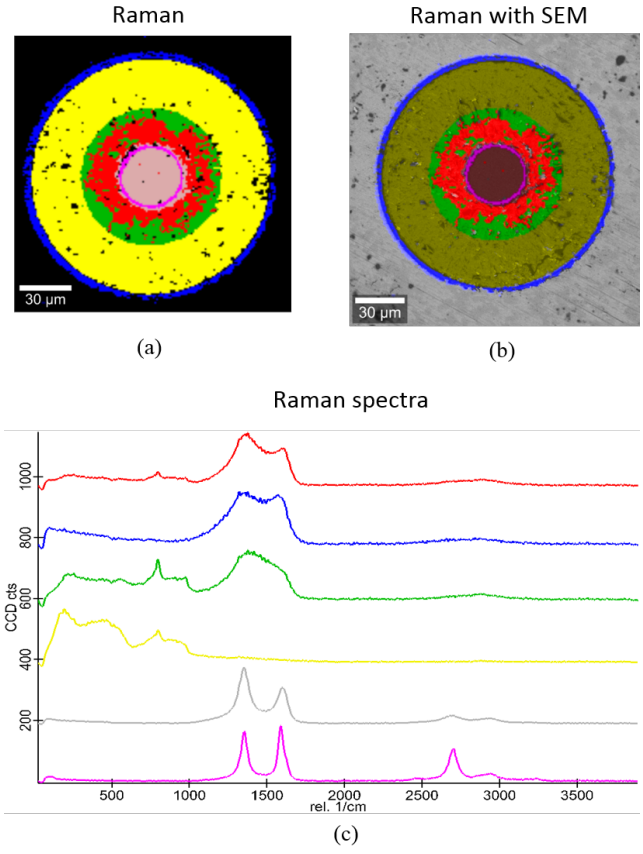

Fig. 4. (a) Raman image of SiC fibre sample (b) composite image by the superposition of SEM image with Raman image. (c) The corresponding color-coded Raman spectra

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The superposition of the SEM image (Fig. 1b) and the colour-coded Raman image (Fig. 4a) allow comparing the ultra-structure with the chemical compound information. The carbon core of ~35μm diameter in the centre is occupied by partly amorphous graphite whereas near the boundary of carbon core and SiC layer, highly crystalline graphite shows up and is visualized by pink line. Multiple phases were indexed near the boundary with a width of ~30μm as red and green bands appear. At the periphery of SiC region in SEM image, only single SiC phase is observed as colored by yellow. The dark carbon-based adhesion interlayer is indexed by blue carbon peak between SiC and the alloy matrix.

B. Micro-focus synchrotron X-ray mapping results

Once sample alignment with the synchrotron X-ray beam was assured, the beam was focused down to a sub-micron spot using a pair of Kirkpatrick-Baez mirrors. The sample was translated to illuminate different locations within the fibre, and 2D diffraction patterns were recorded at each position. Detailed pattern analysis provided information about the preferred orientation of the crystal lattice (texture), interplanar lattice spacing (and hence elastic lattice strain), and peak broadening that is related to the crystallite size and micro-strain.

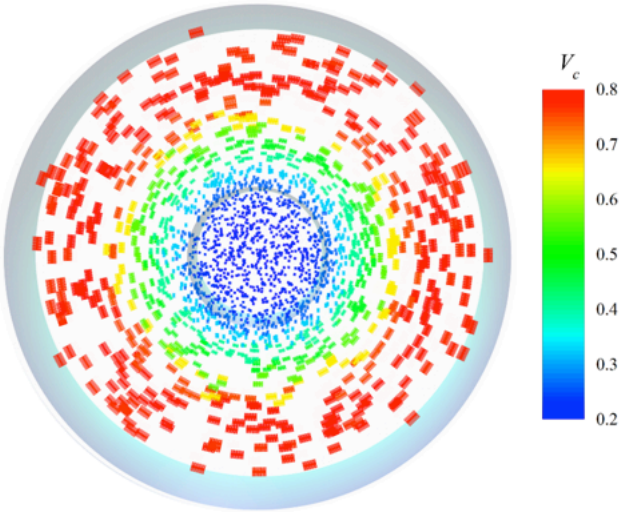

Fig. 5. Schematic diagram of the structure of the carbon filament core, displaying the degree of crystallinity (colour online, refer to the colour bar), and the mean particle size (magnified x1000) and orientation (adapted from [3]).

Here we present only that part of the analysis that is related to the carbon filament core, illustrated diagrammatically in Fig. 5. The ~35μm diameter carbon fibre is characterised by the varying crystalline content V_c that is indicated according to the colour scale shown. The crystallites are shown by the rectangular shapes to reveal their aspect ratios and alignment, and their size is exaggerated a thousand times to ensure visibility. This transition was thought to be associated with the change in the growth mode that occurs during fibre fabrication [3] and is chosen during manufacture to optimise the combination of fibre stiffness and strength.

IV. DISCUSSION AND CONCLUSION

The combined SEM and Raman spectroscopy mapping performed in the present study demonstrated the ability of RISE microscopy to carry out highly spatially resolved characterisation of ultra-structural surface with molecular compound information by fully-integrated SEM and Raman imaging. This is crucial for developing exquisite control over the materials properties and for designing better nano-structurally engineered materials with superior performance.

This was enhanced further by high resolution structural mapping using a micro-focused synchrotron X-ray beam. This represented a significant step forward compared to the already well-established diffraction scanning approach [5] that relies purely on the beam collimation and aims to determine the lattice parameter variation (within the plane perpendicular to the incident beam). The interpretation of multiple diffraction peaks in terms of their intensity and broadening allowed crystallite orientation and size to be mapped at the microscopic length scale.

The combination of several imaging and mapping modes to study the same object represents a form of correlative microscopy approach. In the case considered, it allowed combined characterization of the internal nano-crystalline / amorphous crystal structure of the carbon filament core within the CVD-deposited SCS-6 silicon carbide fibre used as reinforcement within an aerospace titanium alloy matrix composite for bladed disks (“blisks”).

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REFERENCES

[1] A. Vassel, Continuous fibre reinforced titanium and aluminium composites: a comparison, Materials Science and Engineering A, 1999, vol. 263, pp.305-313.
[2] X.J. Ning, P. Pirouz, The microstructure of SCS-6 SiC fiber, Journal of Materials Research, 1991, vol. 6, pp. 2234-2248.
[3] N. Baimpas, A. Lunt, I.P. Dolbnya, et al. Nano-scale mapping of lattice strain and orientation inside carbon core SiC fibres by synchrotron X-ray diffraction. J Prosthet Dent, 2014, vol. 79, pp. 85-92.
[4] J. Jiruše, M. Haničinec, M. Havelka, O. Hollricher, W. Ibach, P. Spizig, Integrating focused ion beam–scanning electron microscope with confocal Raman microscope into a single instrument, Journal of Vacuum Science & Technology B, 2014, vol. 32, pp. 06FC03.
[5] X. Song, M. Xie, F. Hofmann, T.S. Jun, T. Connolley, C. Reinhard, R.C. Atwood, L. Connor, M. Drakopoulos, S. Harding, A.M. Korsunsky, Residual stresses in Linear Friction Welding of aluminium alloys, Materials and Design, 50, p. 360-369, 2013.

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